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Non-radiative transitions of 2-methylindole and 2-methylindoline in presence of the electron acceptor 2-nitrofluorene at the ambient as well as at liquid N_2 temperatures

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Abstract : In the present work, the results of detailed investigations have been reported, both at the ambient temperature and at 77 K, on the fluorescence and phosphorescence quenching of the two electron donors, 2-methylindole(2MI) and 2-methylindoline(2MIN), in presence of the acceptor 2-nitrofluorene(2NF). Both steady state and time-resolved spectroscopic techniques have been used. At the ambient temperature and at very dilute solutions of the donor ($\sim 10^{-4}$ mol dm^{-3}) and acceptor molecules($\sim 10^{-6}$ mol dm^{-3} to $\sim 10^{-5}$ mol dm^{-3}), static quenching process appears to be primarily responsible for the observed fluorescence quenching. However, at higher concentrations of the donors and acceptors ($\sim$ x10^{-3} mol dm^{-3}), dynamic processes, specially photoinduced electron transfer (PET) reactions has been confirmed by the direct observations of the radical ions (both cation and anion) in the transient absorption spectra. PET reactions turn out to be highly exothermic type ($-\Delta G^0_{SET} \geq 2.0$ eV) in highly and moderately polar environments eg., acetonitrile (ACN) and tetrahydrofuran (THF) while in low polarity medium n-heptane (NH), the exothermicity reduces considerably ($-\Delta G^0_{SET} \geq 0.7$ to 0.9 eV). Spectral argument in favour of occurrence of another dynamic process "energy transfer" at the room temperature, was not observed due to lack of fluorescence emission of the acceptor 2NF. At 77K in EtOH rigid glassy matrix the observed quenching of both fluorescence and phosphorescence of the donors by 2NF has been attributed to the presence of static mode since both the fluorescence and phosphorescence decay times of the former species remains unchanged even in presence of the later molecule. The PET, being a thermally activated process, does not have significant role in quenching mechanism at 77K.

Keywords Photoluminescence, static quenching , dynamic process

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1. Introduction

Indole being a chromophore of the amino acid tryptophan, carries extreme biological importance[1-12]. Indoline which lacks a π-bond in the five-membered ring as compared to indole, also carries significant biological importance as it possesses photoreceptor and photochromic properties [13, 14]. In our earlier paper [15], a preliminary study on the solution-phase photophysical properties of 2-methylindole (2MI) and 2-methylindoline (2MIN) were reported. From the steady state absorption spectral measurements, no clear-cut evidence of formation of ground state charge transfer (CT) complex between the present donor (D) and acceptor (A) systems was found. It is anticipated that lack of π-bond in the five-membered ring of 2MIN might make considerable difference in its electron donating capability in presence of a suitable acceptor as compared to 2MI. The present investigation was carried out on the emission quenching phenomena of these compounds in presence of the well-known electron acceptor 2-nitrofluorene (2NF) both at the ambient temperature (296 K) and 77K. An attempt was made to examine whether both static (no lifetime drop) and dynamic (lifetime drop) parts are involved in the above fluorescence quenching phenomena. To have a clear picture regarding the nature of quenching modes involved within these D-A systems, detailed investigations were carried out with these D-A systems in various solvents of different polarity at 296 K as well as in ethanol (EtOH) rigid glassy matrix at liquid N_2 temperature (77K) with the help of both steady state and time-resolved spectroscopic techniques. In the present investigation, all the

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earlier in many quenching studies [17b, 18]. Following the views of Nemzek and Ware[19], the positive deviation could be proposed due to the presence of some kind of static quenching mode. It is well known that there are two types of static quenching: one the ground state complex formation and the other sphere of action model [18]. As very dilute solutions of donor and acceptor molecules (10^{-6} to 10^{-5} mol dm^{-3}) were chosen, the static quenching phenomena observed in the present case could not be described by the latter model. Now, to examine whether ground state complex is formed within the reacting systems, a systematic study on the electronic absorption spectra of 2MI (2MIN) were made in presence of 2NF

Figure 3 reproduces the electronic absorption spectra of the mixture of the donor 2MI and the acceptor 2NF in ACN solvent. The spectra show the superposition of the individual absorption spectra of these reacting species. However, it is very difficult to rule out the possibilities of ground state complex formation inspite of lack of its clear evidence as the spectra of both the donor and acceptor are extensively overlapped.

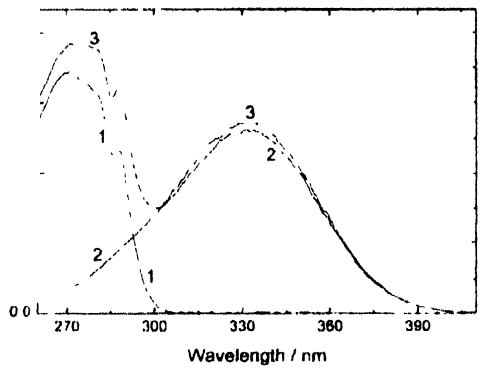

Figure 3. Electronic absorption spectra of 2MI (curve 1), 2NF (curve 2) and the mixture of 2MI and 2NF in ACN at ambient temperature (curve 3) Concentration of the donor 2MI in ACN 1.9×10^{-4} mol dm^{-3} Concentration of the acceptor 2NF in ACN 2.9×10^{-5} mol dm^{-3} The mixture in ACN contains the above concentrations of the donor and the acceptor

Thus from the above steady state measurements, it appears that the fluorescence quenching of the donors 2MI/2MIN in presence of the acceptor 2NF proceeds primarily through static process even when their concentrations are very low (10^{-6} to 10^{-5} mol dm^{-3}). As both 2MI and 2MIN are known to be good electron donors and 2NF is a well-known accepting species[15], occurrence of dynamic process *eg*, photoinduced electron transfer reaction (PET) in these reacting species could not be ruled out. However, from the transient absorption measurements by laser flash photolysis technique, it is observed that electron transfer (ET) does really occur (vide infra). However, to observe transient products(cations and anions) formed during ET reactions, higher concentrations($\sim 10^{-3}$ mol dm^{-3}) of the donor and accepting species were required. Before going into the details of the results obtained from the transient absorption measurements, we would discuss about the possibility of occurrence of such a basic nonradiative process from the thermodynamical point of view *i.e.*, by measuring the redox potentials of the reacting partners by cyclic voltammetry. The details are given below.

3.3. Possibility of Photoinduced ET reactions at 296 K :

In ACN fluid solution, the possibility of the occurrence of photoinduced ET reactions from the singlet (S_1) excited donor to the ground state acceptor can be predicted by computing the free energy change of ET reactions from the well-known Rehm Weller relation [20, 21]

$$\Delta G^0_{SET}(ACN) = E^{OX}_{1/2}(D/D^+) - E^{RED}_{1/2}(A^-/A) - E^*_{0,0} - C, \qquad (2)$$

where $E^{OX}_{1/2}(D/D^+)$ is the half-wave oxidation potential of the donor and $E^{RED}_{1/2}(A^-/A)$ is the half-wave reduction potential of the acceptor, both measured in ACN solvent at 296 K $E^*_{0,0}$ is the excitation energy of the first singlet state (S_1) of the donor $C = e^2/(4\pi\varepsilon_0\varepsilon_s R)$ is the Coulomb stabilization energy which accounts for the stabilization of the ion pair compared to the free ions due to the proximity of oppositely charged ions. R is the D-A center-to-center separation distance and other symbols have their usual meanings. The term C is often neglected in highly polar solvent ACN as its contribution in such environment is very low (~ 0.06 eV)[22]. Table 2 shows that ET reactions from the excited singlet of the present donors to the ground state acceptor in ACN solvent is highly exothermic, as evident from large negative values of ΔG^0_{SET} ($\Delta G^0_{SET} << 0$) and hence occurrences of such reactions are favorable from the thermodynamical point of view. On the other hand, ET reactions between the present D-A pairs in their ground states have a poor probability to occur due to positive values of ΔG^0_{SET}

Table 2. Redox potentials and Gibbs free energies (ΔG^0_{SET}) for the present D-A systems at 296 K

[a]D–A system	[b]$E^{OX}_{1/2}(D/D^+)$ (V)	[b]$E^{RED}_{1/2}(A/A^-)$ (V)	$E^*_{0,0}$ (eV)	ΔG^0_{SET} (eV)
2MI*+2NF+ACN	0.984	−1.175	4.28	−2.12 (+2.16)
2MIN*+2NF+ACN	0.610	−1.175	4.13	−2.34 (+1.79)
2MI*+2NF+THF	0.984	1.175	4.28	−1.91 (+2.37)
2MIN*+2NF+THF	0.610	−1.175	4.13	−2.13 (2.00)
2MI*+2NF+NH	0.984	−1.175	4.28	−0.70 (+3.58)
2MIN*+2NF+NH	0.610	1.175	4.13	−0.92 (+3.21)

[a] * denotes the first excited singlet (S_1). [b] Redox potentials measured in ACN fluid solution at 296 K Values of ΔG^0_{SET} shown in parentheses correspond to the ground state.

As we cannot measure redox potentials of the reactants in the other solvents used in the present investigation *viz.*, THF and NH, we computed the shift in the free energy change

associated with the ET reactions within the present D-A systems on going from ACN to THF/NH due to solvation effect by using the following relation.

$$\Delta G^0_{SET}(\text{THF}/n-\text{heptane}) = \Delta G^0_{SET}(\text{ACN}) + \Delta E - C, \quad (3)$$

where ΔE is given by

$$\Delta E = \Delta G^0_{solv}(\text{ACN}) - \Delta G^0_{solv}(\text{THF}/n-\text{heptane}). \quad (4)$$

Following Kavarnos and Turro [23], the solvation energy was computed by using the relation 5.

$$\Delta G^0_{solv} = -\frac{e^2}{2}\left(\frac{1}{r_D} + \frac{1}{r_A} \qquad \varepsilon_s \right. \quad (5)$$

Here, the symbols have their usual meanings. The Coulomb stabilization term (C) was chosen to be 0.1 eV and 0.2 eV for THF and n heptane (NH) solvents, respectively following the Weller assumption[24, 25]. The values of free energy change, computed for the present D-A systems in THF and NH solvents, are shown in Table 2. From the observed negative values of ΔG^0_{SET} it seemingly indicates that the possibility of ET reactions between the present D-A systems still retains in these solvents also, as it was seen in the other solvent ACN. However, in the case of singlet excited donor - ground state acceptor systems the exothermicity decreases with decreasing polarity of the solvent as expected.

3.3a Transient absorption spectroscopy

For experimental verification of occurrence of photoinduced ET reactions within the present donor-acceptor systems pulsed laser excitation 355 nm, using Nd YAG laser system, was used to excite specifically the acceptor moiety dissolved in the mixture of the donor 2MI (or 2MIN) and ACN. The transient absorption spectra of the mixture of 2MI and 2NF is shown in the Figure 4 at three different delay times between the exciting and analyzing pulses. At 0.5 μs delay a prominent band at 400 nm is observed which is well-known to be due to triplet-triplet transitions of 2NF [22]. Two additional bands, relatively weak, appear around 480 nm and 550 nm regions. The latter band system seems to be due to indolyl cationic species[26]. To confirm whether the 480 nm band corresponds to the band of the acceptor anion, metallic sodium(Na) experiment was performed separately. Interestingly in the electronic absorption spectra of the acceptor 2NF in the presence of metallic sodium, a new band appeared in the 480 nm region. This band gradually disappears in the presence of molecular oxygen. This experiment clearly demonstrates that the 480 nm band observed in transient absorption spectra of the mixture of 2MI and 2NF is due to the formation of 2NF anion. Thus from the transient absorption measurements, it was proved unequivocally that the PET reactions do occur among the reacting species studied in the present investigation.

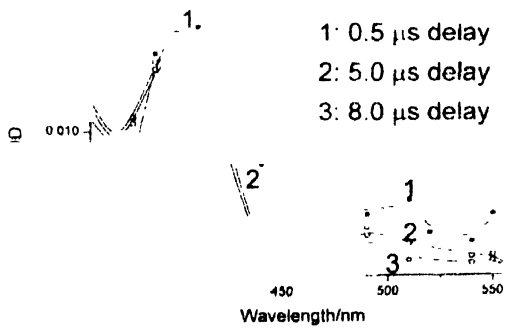

Figure 4. Transient absorption spectra of the mixture of 2MI and 2NF in ACN at the ambient temperature. The delays used are shown in the figure. Concentrations of both the reacting species (~ $\times 10^{-3}$ mol dm^{-3})

3.3b Analysis of the rates associated with electron transfer reactions

Next, we computed the rates associated with the ET reactions among the present singlet excited donors and the ground state acceptor 2NF. According to semi-classical Marcus theory, the first-order forward ET rate constant under non-adiabatic conditions can be written in the general form of eq. (6a) [27-29]

$$k_{ET}(R) = \frac{}{\hbar\lambda_v(R)k_BT} |V(R)|^2 \sum^{\infty} \left(e^{-S} S^v / v!\right) \exp \frac{\left(\Delta G^0_{SET} + \lambda_v(R) + v\hbar\nu\right)^2}{4\lambda_v(R)k_BT} \quad (6a)$$

where $S = \lambda_v / h\nu$. (6b)

Here, V(R) is the exchange interaction energy for a D-A separation of R, S is the reduced displacement parameter between the potential surfaces of the reactant and product complexes; $\lambda_v(R)$ is the solvent reorganization energy and λ_v is the vibrational reorganization energy. The total reorganization energy (λ) is the sum of solvent and molecular contributions. The vibrational modes associated with λ_v are treated quantum mechanically and it is assumed that the frequency of these modes can be represented by a single average frequency ν. In the present investigations, we have chosen fixed values for λ_v and ν of 0.3 eV and 1500 cm^{-1}, respectively. These values of λ_v and ν were chosen earlier by several authors [22] to compute k_{ET} values as these are the characteristic values for aromatic D-A systems [22, 29,30]. Eq.(6a) represents the overall ET rate constant results from a summation of the rate constants of ET from the donor to the different vibrational levels(v) of the acceptor.

Within the framework of dielectric continuum model, λ_s is expressed as [22]

$$\lambda_s(R) = \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{r_D} + \frac{1}{r_A} - \frac{2}{R}\right) \quad (7)$$

where the symbols have their usual meanings. The radii (r_D and r_A) were computed from molecular volume of the neutral molecule [31] according to the equation shown below :

$\frac{4\pi r^3}{3} = \frac{M}{N_A \rho}$, where the symbols have their usual meanings.

The ET rate constant given by eq. (6a) depends on the D-A separation distance R mainly through the exchange interaction energy $V(R)$, and the solvent reorganization energy, λ_s in a polar solvent like ACN. The exchange interaction energy depends on R approximately exponentially and may be expressed as [32]

$$V(R) = V_0 \exp\left[-\{\beta(R - r_D - r_A)/2\}\right], \quad (8)$$

where V_0 is the exchange interaction energy at $R = r_D + r_A$ (Van der Waals contact distance) and β is its attenuation coefficient with R.

It is important to note that eq. (6a) gives the first-order ET rate constant for a D-A pair with a fixed separation R. In the present intermolecular studies, both the donors and acceptors move randomly and ET reaction occurs between the donor and acceptor molecules distributed randomly throughout the solution. In this situation, the distance between the donor and acceptor, is not fixed, but variable. According to Kikuchi [33], highly exothermic ET reactions ($\Delta G^0_{SET} < -2.0$ eV) should occur at R = 7 Å. Based on this, we calculated the ET rate constant in some of our earlier works [34-36] by making a crude assumption of R = 7 Å. In order to have a better knowledge about the distance of separation (R) between the donor and acceptor molecules involved in ET reactions, the distance dependence of the Marcus first-order ET rate constant was computed by using eq. (6a) (Figure 5) following the procedure adopted by Tachiya *et al* [37, 38]. Figure 5 shows that for the present D-A systems, ET reaction rate (k_{ET}) becomes largest at the Van der Walls contact distance and as the value of R increases, ET reaction rate decreases monotonically. So it can be presumed that with the present D-A pairs, ET reactions are occurring mostly at the Van der Waals contact distance. Therefore, the ET rate constants for the present D-A systems were computed from eq. (6a) by assuming R to be equal to the Van der Waals contact distance ($= r_D + r_A$).

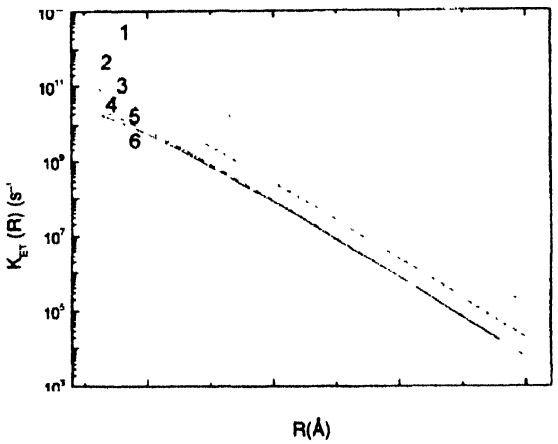

Figure 5. First-order ET rate constant ($k_{ET}(R)$) as a function of D-A separation distance (R) for the present D-A systems at 296 K. (1) : 2MI + 2NF + n-heptane; (2) : 2MIN + 2NF + n-heptane; (3) 2MI + 2NF + THF; (4) : 2MI + 2NF + ACN; (5) : 2MIN + 2NF + THF; (6) : 2MIN + 2NF + ACN.

Finally, one has to make sure in using eq. (6a) that the ET reaction studied is really non-adiabatic. The non-adiabaticity of an ET reaction can be tested by computing the adiabatic parameter (A) defined by [22]

$$A = 4\pi |V(R)|^2 e^{-3} \tau_l / \lambda_s(R) \hbar, \quad (9)$$

where τ_l is the longitudinal solvent relaxation time equal to 0.2 ps in ACN [27]. For A ≪ 1, the ET process is non-adiabatic and its rate can be computed by using eq. (6a). For the present D-A systems in ACN solvent, A ~ 10^{-2} and so it seems that ET reactions in the present D-A systems are of non-adiabatic type in ACN solvent. As the proper value of τ_l in THF or n-heptane is not known, we could not compute the value of A in these solvents. However, the ET reactions in the present D-A pairs in these solvents were also assumed to be non-adiabatic as in the solvent ACN.

Figure 6 shows that irrespective of solvent polarity, the general trend of the ET reactions occurring in the present D-A systems is to follow Marcus inverted region, *i.e.*, the first-order ET rate decreases with increasing exothermicity. Since the occurrence of forward ET reactions in the inverted region is rare, further investigations are needed to draw a definite conclusion regarding the true nature of ET reactions in the present D-A systems.

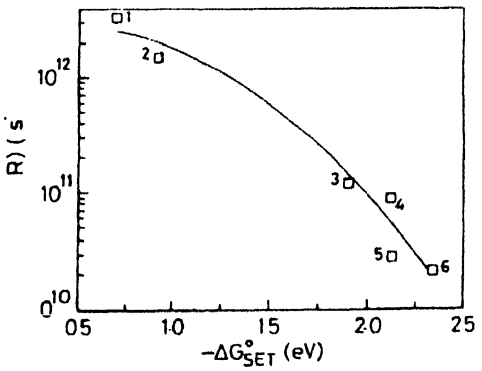

Figure 6. First-order ET rate constant ($k_{ET}(R)$) as a function of the free energy change associated with excited singlet (S_1) ET reactions ($-\Delta G^0_{SET}$) for the present D-A systems at 296 K. (1) . 2MI + 2NF + n-heptane (2) : 2MIN + 2NF + n-heptane ; (3) : 2MI + 2NF + THF; (4) . 2MI + 2NF + ACN; (5) . 2MIN + 2NF + THF; (6) : 2MIN + 2NF + ACN.

From the values of k_{ET} (Table 1), 2MI seems to be a better electron donor than 2MIN. This is quite consistent with the predictions made in our earlier paper [15] based on the probable canonical structures of 2MI. It was shown from these canonical structures that besides the nitrogen atom, there are three other

sites in the molecule which are electron-rich and can act as donor sites. On the other hand, in the molecule 2MIN, the π-system not being extended unlike the case of 2MI, such canonical structures are precluded.

3.4. Quenching phenomena at 77 K :

In EtOH rigid glassy matrix at 77 K, both the fluorescence and phosphorescence intensities of the present donors (2MI/2MIN) are quenched regularly with gradual addition of the acceptor 2NF (Figures 7(a)-(b)). With the addition of 2NF, values of the fluorescence lifetime τ_f and the phosphorescence lifetime τ_p of the present donors do not alter appreciably (within experimental error). This seemingly indicates that at 77K, the observed quenching could be due to the involvement of static quenching mode and the possibility of occurrence of any dynamic process *eg.*, photoinduced electron transfer is very slim. This observation conforms to our expectation that the electron transfer reaction being a thermally activated process is

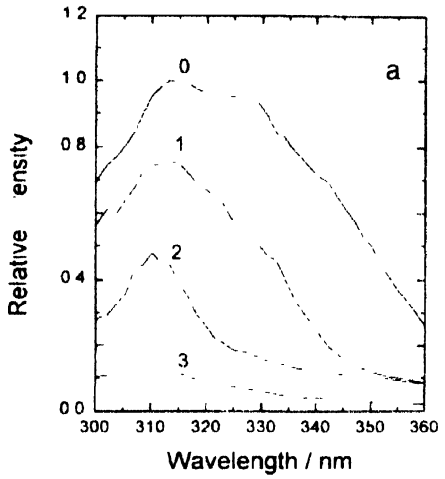

Figure 7a. Fluorescence emission spectra of 2MI (C = 1.5 × 10^{-4} mol dm^{-3}) in EtOH rigid glassy matrix at 77 K (λ_{exc} = 280 nm) in presence of 2NF. Concentrations of 2NF (mol dm^{-3}) : (0) 0, (1) 1.0 × 10^{-4}, (2) 3.1 × 10^{-4}, (3) 4.1 × 10^{-4}

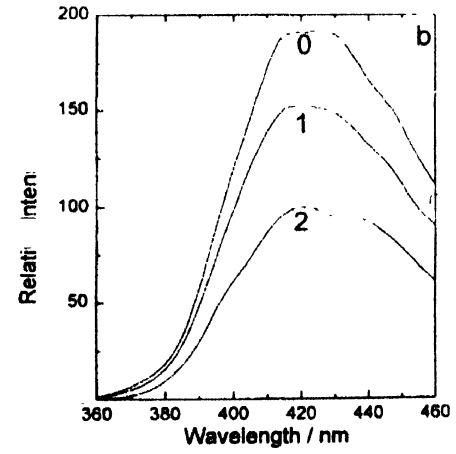

Figure 7b. Phosphorescence emission spectra of 2MIN (C = 2.3 × 10^{-4} mol dm^{-3}) in EtOH rigid glassy matrix at 77 K (λ_{exc} = 300 nm) in presence of 2NF. Concentrations of 2NF (mol dm^{-3}) : (0) 0; (1) 2.6 × 10^{-5}, (2) 1.3 × 10^{-4}.

expected to have much less effect on the emission quenching of the donors at 77 K compared to that at room temperature [39,40]

4. Concluding remarks

From the present investigation, the following conclusions have been drawn

(1) At the ambient temperature, the fluorescence quenching of the present donors in the presence of 2NF, results primarily from the static process when the concentrations of the reacting species are very low (~10^{-6} – 10^{-5} mol dm^{-3}). Though the exact mechanism of the static mode is not very clear at the present stage of investigation, but the possibility of ground state complex formation could not be ruled out. At much higher concentrations (~ 10^{-3} mol dm^{-3}) of the donor and acceptor, the existence of photoinduced ET reactions in these systems was directly observed from the transient absorption spectral measurements by laser flash photolysis techniques. The ΔG^0_{ET} value which is a measure of exothermicity of the ET reaction is found to decrease with the lowering of the dielectric constant of the surrounding medium. The forward ET reactions seem to occur in the Marcus inverted region, though further investigations are needed before making any definite conclusion. Moreover, 2MI seems to possess better electron donating capability than 2MIN as expected.

(2) In EtOH rigid glassy matrix at 77 K, the observed donor fluorescence and phosphorescence quenching in the presence of the acceptor (quencher) 2NF is attributed to be due to the presence of primarily static quenching mode since the lifetimes of both the emission processes of the donors, used in the present investigation, remains unaltered even in presence of the quencher 2NF.

Acknowledgments

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